Supporting Information

Bubble-Propelled Micromotors for Enhanced Transport of Passive Tracers

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Supporting Videos:

Video 1. Bubble-propelled micromotors enhancing the transport of 2 μm passive tracers and compared to their Brownian motion.

Video 2. Freely-swimming *vs* bubble-generating fixed micromotors.

Video 3. Effect of different types of micromotors (bubble-propelled, nanowires and Janus particles) on the enhanced transport of passive tracer particles.

Video 4. Effect of the bubbles (alone, without motion) on the enhanced transport of passive tracer particles.

Video 5. Influence of the density of the micromotors upon the transport of passive tracer particles.

Experimental Section

Synthesis of micro-/nano motors

Microtubes were prepared using a common template directed electrodeposition protocol. First, a 75 nm gold film was sputtered on one side of a cyclopore polycarbonate membrane template containing 2 µm double-cone-shaped micropores (catalog No 7060-2511; Whatman, Maidstone, U. K.) to serve as a working electrode. The sputter was performed at room temperature by using a Denton Discovery 18 sputter system, under vacuum of $5X10^{-6}$ Torr, DC power of 200 W and flow Ar to 3.1 mT, with a rotation speed of 65 rpm and a sputter time of 90 s. Secondly, the membrane was assembled in a plating cell with an aluminum foil serving as a contact electrode and PEDOT was electropolymerized in the membrane from a plating solution containing 7.5 mM EDOT and 7.5 mM COOH-EDOT, 7.5 mM KNO_3 and 100 mM sodium dodecyl sulfate (SDS); using a charge of 0.06 C and a potential of +0.80 V (*vs.* a Ag/AgCl reference electrode, along with a Pt-wire counter electrode). Thirdly, the inner platinum tube was deposited galvanostatically at 2 mA for 600 s. Subsequently, the gold layer was removed by hand polishing with 3-4 mm alumina slurry and the membrane was then dissolved in methylene chloride for 10 min to completely release the microtubes. Finally, the microtubular engines were collected by centrifugation at 6000 rpm for 3 min and washed repeatedly with methylene chloride, followed by ethanol and ultrapure water (18.2 MΩ cm), three times for each, with a 3 min centrifugation following each wash.

The Au/Pt nanowire motors (2x0.2 µm) were prepared by electroplating the corresponding metals into the micropores of a porous alumina membrane template (catalog no. 6809-6022; Whatman, Maidstone, U.K.). A thin Ag film was sputtered on the branched side of the membrane to serve as a working electrode. A sacrificial Ag segment was firstly electrodeposited into the branched area of the membrane using a silver plating solution (1025 RTU@4.5 Troy/Gallon; Technic Inc., Anaheim, CA) and a total charge of 3 C at -1 V (*vs* Ag/AgCl). This was followed by an electroplating of gold (1.5 C) from a gold plating solution (Orotemp 24 RTU RACK; Technic Inc.) at -1 V (*vs*

Ag/AgCl). Subsequently, platinum was deposited galvanostatically at -2 mA for 50 min from a platinum plating solution (Platinum RTP; Technic Inc.). The sputtered Ag layer and sacrificial Ag segment were simultaneously removed by mechanical polishing using cotton tip applicators soaked with 8 M HNO_3 for ca. 5 min to ensure complete silver dissolution. The bisegment Au/Pt nanowires were then released by immersing the membrane in 3 M NaOH for 30 min. These nanowires were collected by centrifugation at 10000 rpm for 5 min and washed repeatedly with nanopure water (until a neutral pH was achieved).

SiO_2-Pt Janus particles were prepared using silica microparticles (1.21 μm mean diameter, Bangs Laboratories, Fishers, IN, USA) as the base particles. 20 μL of silica particles solution were first dispersed into ethyl alcohol (A407-4, Fisher, Pittsburgh, PA, USA) and centrifuged. Then, the silica particles were re-dispersed in 200 μL ethyl alcohol. The sample was then spread onto glass slides and dried uniformly to form particle monolayers. The particles were sputter-coated with a 20 nm Pt layer using the Denton Discovery 18 unit. The deposition was performed at room temperature with a DC power of 200 W and an Ar pressure of 2.5 mT for 15s. In order to obtain a uniform Janus half-shell coating, rotation was turned off and the sample slides were set up at an angle to be parallel to the Pt target. After the fabrication, the Janus particles were detached from the substrate via sonication or pipette pumping.

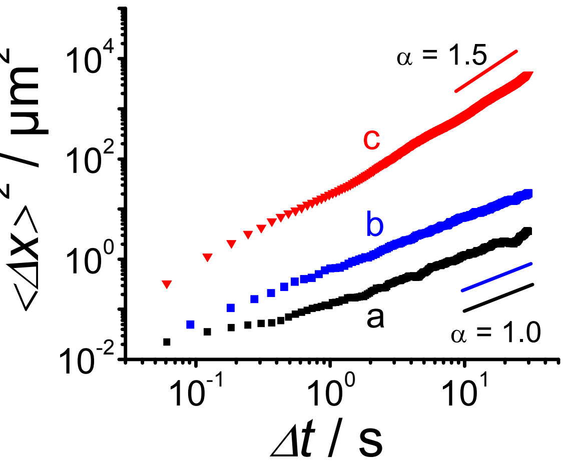
Commercial polystyrene particles of 2.077 μm, 2.81% solids and $5.68X10^9$/ml (catalog No 19814, Polysciences, USA) were used as tracers. A fresh stock solution was prepared daily by dissolving 1 μl of commercial solution in 99 μl of D.I water.

Equipment

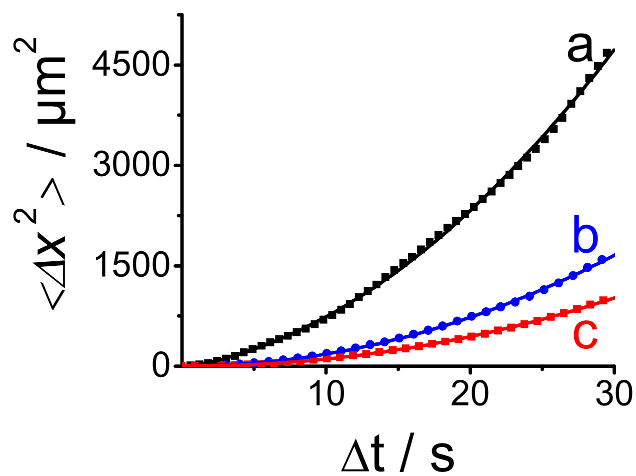
Template electrochemical deposition of microtubes was carried out with a CHI 661D potentiostat (CH Instruments, Austin, TX). To investigate particle motion, we captured movie clips of the particles (30 s, 16 frames per sec) using an optical microscope (Nikon Instrument Inc. Ti-S/L100) and a digital camera (Photometrics QuantEM 512/SC, Roper Scientific, Duluth, GA). Following particle tracking and analysis of the video clips with MetaMorph 7.6 software (Molecular Devices, Sunnyvale, CA), the mean square displacement ($<\Delta x^2>$) for each particle (100 particles per each experiment) was calculated as a function of time.

Experiments

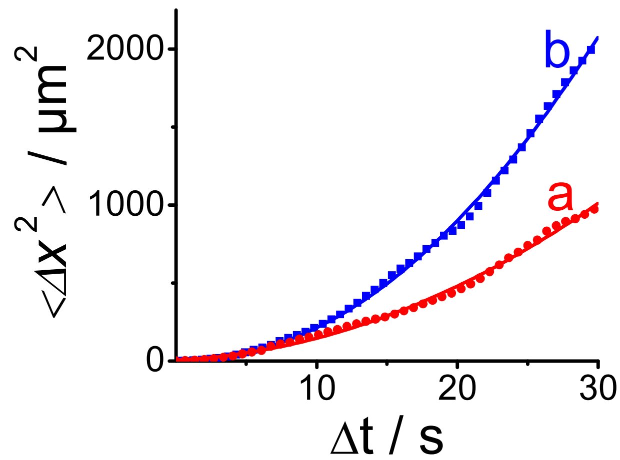
For experiments with swimming micromotors, 1 μL of each (particles solutions, Triton-X-100, microtubular engines or Au-Pt nanowires or SiO_2-Pt Janus particles (either at 1X and 2X densities) and prepared daily H_2O_2 solutions (Sigma-Aldrich, cat. 95313) were placed onto a glass slide. The final concentrations are $1.4X10^7$/ml particle tracers, $4X10^6$/ml active micromotors, 5% Triton X-100 (for experiments with microtubular engines only) and increasing concentrations of H_2O_2 ranging from 1.0 to 1.5%. To study the pure Brownian motion, 1 μL of aqueous solutions of suspended 2 μm PS particles and microtubular engines were placed on the surface of a glass slide with 5% Triton X-100 as surfactant. Control experiments were run with the drops contained into the reservoir of a tailor-made PDMS chip. To investigate the effect of the bubble generation alone on the motion of particles, we functionalized a glass slide with the cationic polymerized amino acid polylysine as follows. The glass slide was first cleaned with a 1 M NaOH solution, washed with deionized water and dried with air. A positively modified surface was later formed on the negatively charged cleaned glass slide, by immersing it in a commercial 0.1% polylysine solution for 20 min. After this time, the microtubular engines were attached to the glass slide by electrostatic interaction between their surface carboxy moieties and the exposed positive charges of the glass slide.



S.I. Figure 1. Effect of surfactant on the enhanced transport of passive tracers. Log-log plot of mean-squared displacements of 100 passive tracers traveling only by Brownian motion in the presence (a) and in the absence (b) of surfactant. In comparison, displacements of tracers subjected to the effect of active micromotors swimming in the presence of 5% Triton X-100 surfactant and 1.5% H_2O_2 fuel (c), necessary for active motors self-propulsion.



S.I. Figure 2. Effect of different self-propelled motors on the enhanced transport of passive tracers. Nanowires (b) and Janus particles (c), at 5% H_2O_2, compared to bubble-propelled motors (a) at 1.5% H_2O_2.



S.I. Figure 3. Effect of microtubes density on the enhanced transport of passive tracers. (a) $4X10^6$/ml and (b) $8X10^6$/ml, 1% H_2O_2 and 5% Triton.